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(54) **Antifouling paint composition**

(57) An antifouling paint composition comprises as a film-forming component a vinyl-tape copolymer obtained by copolymerization of

(A) 1 to 50% by weight of a specific polymerizable unsaturated polysiloxane compound,

(B) 0 to 30% by weight of a specific polymerizable unsaturated alkoxy silane compound, and

(C) 20 to 99% by weight of a polymerizable unsaturated vinyl monomer other than the compounds (A) and (B) above.

The composition may also comprise a siloxane having primary hydroxyl groups at both ends of the molecule.

GB 2 192 400 A

SPECIFICATION

Antifouling paint composition

5 This invention relates to an antifouling paint composition, and more specifically, to a nontoxic antifouling paint composition designed to prevent adhesion of aquatic organisms to the submerged parts of ships and marine structures. 5

Heretofore, paints containing cuprous oxide or organotin compounds have been coated on the submerged parts of ships or marine structures with significant effects of preventing adhesion of aquatic organisms. However, since toxic substances such as copper compounds or organotin compounds dissolve from the coatings and cause environmental pollution, it has been desired to develop nontoxic antifouling paints free from toxicants such as copper compounds or organotin compounds. 10

Nontoxic antifouling paints have previously been suggested as seen, for example, from Woods Hole Oceanographic Institution: "Marine Fouling and Its Prevention", Annapolis, Maryland, U.S. Naval Institute (1952) which suggests a possibility of paraffins or waxes being used as a nontoxic antifouling paint, or R. E. Baier, "Prospect for Nontoxic Fouling Resistant Paints", Proc. Annu. Conf. Mar. Technology Soc. (1973) which suggests that fouling resistance can be imparted to the surface of a substrate by providing a coated layer containing both methyl and hydroxyl groups. 15 20

U.S. Patents Nos. 3702778, 4098925, and 4234340 disclose nontoxic antifouling paints which, however, are inferior to the conventional paints containing cuprous oxide or organotin compounds and are still desired to be improved.

The present inventors have therefore worked extensively in order to develop a nontoxic antifouling paint which does not contain a toxicant such as a metal compound or an organometal compound, the cause of environmental pollution, and has antifouling property comparable to conventional antifouling paints containing such toxicants. As a result, they have found that the tendency of aquatic organisms to adhere to paint films is smaller when the coated films have a lower surface energy or contain less polar components or when water droplets dropped onto the surfaces of the paint films, they are easier of falling, and that in such situations, aquatic organisms which may adhere to the coated films are only with a weak adhesion force. The inventors have developed a specific film-forming component which takes advantage of this fact. 25 30

Thus, according to this invention, there is provided an antifouling paint composition comprising as a film-forming component a vinyl-type copolymer obtained by copolymerization of

35 (a) 1 to 50% by weight of a polymerizable unsaturated polysiloxane compound represented by the general formula 35



45 wherein 45

X_1 represents a group of the formula



where R_6 represents a hydrogen atom or a methyl group;

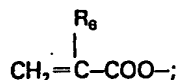
R_1 , R_2 , R_3 and R_4 are identical or different and each represents an alkyl group having 1 to 4 carbon atoms, an aryl group or an aralkyl group; 55

R_5 represents an alkyl group having 1 to 4 carbon atoms, or a hydroxyalkyl group having 1 to 3 hydroxyl groups and 1 to 6 carbon atoms;

a is 0 when X_1 represents the group



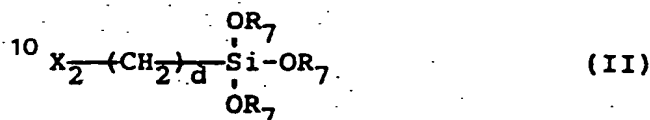
and an integer of 1 to 5 when X_1 represents the group



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and b is a number of 3 to 1,000, (B) 0 to 30% by weight of a polymerizable unsaturated alkoxy silane compound represented by the general formula

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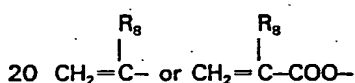


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15 wherein

X_2 represents a group of the formula

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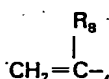


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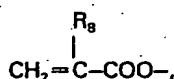
where R_6 represents a hydrogen atom or a methyl group;
 R_7 represents an alkyl group having 1 to 4 carbon atoms; and
 d is 0 when X_2 represents the group

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30 and an integer of 1 to 5 when X_2 represents the group

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and (C) 20 to 99% by weight of a polymerizable unsaturated vinyl monomer other than the compounds (A) and (B) above.

The antifouling paint composition of this invention does not release a toxicant into water. A paint film from the composition has a low surface energy, and its surface permits easy falling of water droplets. Hence, the paint film from the antifouling paint composition of this invention has excellent fouling resistance, and even when organisms adhere to it, they can be easily removed. The antifouling paint composition of this invention exhibits antifouling property comparable to conventional antifouling paints of the type which release toxicants such as metallic compounds or organometallic compounds.

45 In the present specification and claims, the "alkyl group" denotes a linear or branched-alkyl group, and includes, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, n-pentyl and n-hexyl groups. The "aryl group" includes, for example, phenyl, tolyl, xylyl and naphthyl group. Examples of the "aralkyl group" are benzyl and phenethyl groups.

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The principal components constituting the anti-fouling paint composition of this invention are specifically described below.

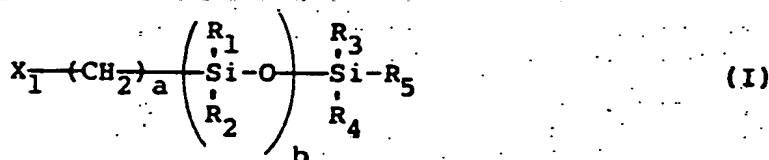
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(A) Polymerizable unsaturated polysiloxane compound

The polymerizable unsaturated polysiloxane compound (A) which is a constituent of the vinyl-type copolymer in the antifouling paint composition of this invention is represented by the following general formula

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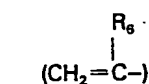
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wherein X_1 , R_1 , R_2 , R_3 , R_4 , R_5 , a and b are as defined above. This polysiloxane compound has a polymerizable vinyl group

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at one end.

In formula (I), R_1 , R_2 , R_3 and R_4 are identical or different and each represents an alkyl group having 1 to 4 carbon atoms, an aryl group or an aralkyl group. The alkyl group, especially a methyl group, is preferred because the surface of a paint film prepared from the resulting vinyl-

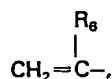
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type copolymer has the lowest surface energy. R_5 represents an alkyl group having 1 to 4 carbon atoms, or a hydroxyalkyl group having 1 to 3 hydroxyl groups and 1 to 6 carbon atoms. The hydroxyalkyl group is preferred because when R_5 is the hydroxymethyl group, the resulting paint composition of this invention gives a coated surface containing both methyl and hydroxyl groups as suggested by R. E. Baier stated hereinabove. Examples of such a hydroxyalkyl group are hydroxymethyl, 2-hydroxyethyl, 1-hydroxyethyl, 1,2-dihydroxyethyl, 3-hydroxypropyl, 2,3-dihydroxypropyl, 1,2,3-trihydroxypropyl, 4-hydroxybutyl, 3,4-dihydroxybutyl, 5-hydroxypentyl, 4,5-dihydroxypentyl, 4,5-dihydroxy-4-methyl-pentyl and 4,4,5-trihydroxypentyl groups.

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When X_1 represents a group of the formula

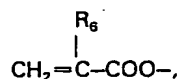
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a is 0, or in other words, X_1 is directly bonded to Si without the intermediary of $-(CH_2)-_a$. When X_1 represents a group of the formula

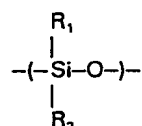
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a is an integer of 1 to 5, preferably 2 to 4.

The b in formula (I) represents the average degree of polymerization of siloxane units

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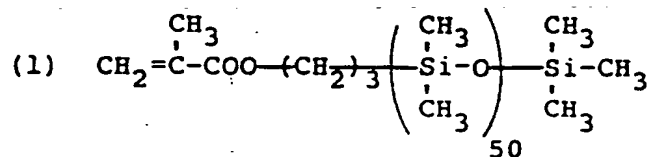


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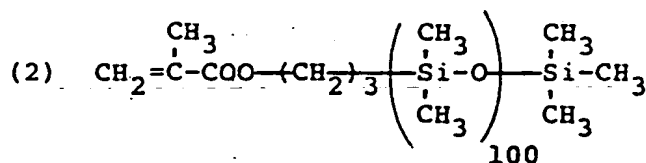
and is a number in the range of 3 to 1,000, preferably 30 to 500, more preferably 50 to 300. The average degree of polymerization is determined by gel permeation chromatography.

Specific examples of the polymerizable unsaturated siloxane compound (a) preferably used include the following compounds.

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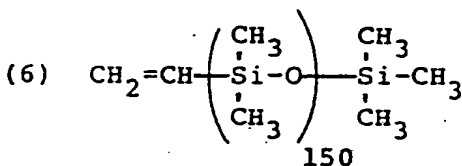
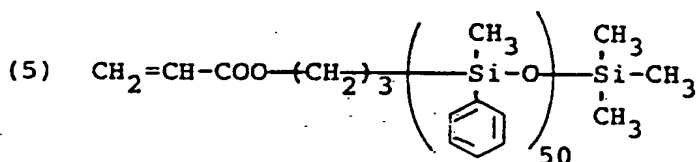
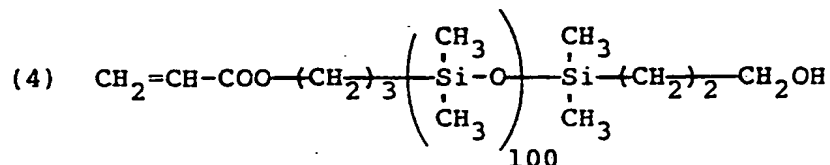
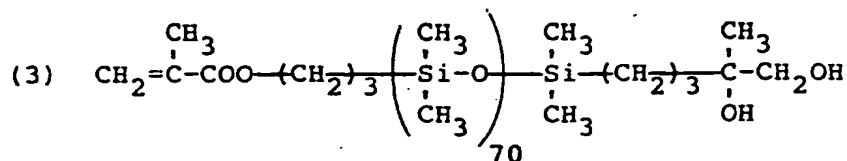
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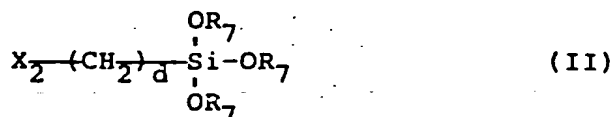
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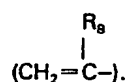
Of these, compounds (1) and (2) are preferred because of ready availability.

(B) Polymerizable unsaturated alkoxy silane compound

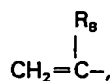
The unsaturated alkoxy silane compound (B) as a constituent of the vinyl-type copolymer in the paint composition of this invention is an alkoxy silane compound of the following general formula



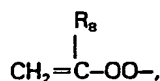
wherein X_2 , R_7 and d are as defined above, and containing a polymerizable vinyl group



In formula (II), the C_1 - C_4 alkyl group represented by R_7 is preferably a methyl group. When X_2 represents the group



d is 0, in other words, X_2 is directly bonded to Si. When X_2 represents the group



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d is an integer of 1 to 5, preferably 2 to 4.

Specific examples of the polymerizable unsaturated alkoxy silane (B) represented by formula (II) include vinyltrimethoxysilane, vinyltriethoxysilane, vinyltripropoxysilane, vinyltributoxysilane, (meth)acryloxymethyltrimethoxysilane, (meth)acryloxyethyltrimethoxysilane, (meth)acryloxypropyltrimethoxysilane, (meth)acryloxypropyltriethoxysilane, (meth)acryloxyethyltriethoxysilane, and (meth)acryloxypropyltributoxysilane. Of these, (meth)acryloxypropyltrimethoxysilane is especially preferred.

(C) Polymerizable unsaturated vinyl monomer

The polymerizable unsaturated vinyl monomer (C) other than the compounds (A) and (B), another constituent of the vinyl-type copolymer in this invention may be any vinyl monomer which polymerizes with the compound (A) and/or the compound (B) in the presence of radicals to give a film-forming polymeric substance. Generally, the monomer (C) is preferably a compound having 1 or 2 (preferably 1) radical-polymerizable alpha, beta-ethylenically unsaturated bond.

Typical examples of the polymerizable unsaturated vinyl monomer (C) are given below.

(a) (C₁-C₁₂ Alkyl) esters of (meth)acrylic acid such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, isopropyl (meth)acrylate, butyl (meth)acrylate, hexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, octyl (meth)acrylate and lauryl (meth)acrylate.

(b) Hydroxy (C₂₋₆alkyl) esters of (meth)acrylic acid such as 2-hydroxyethyl (meth)acrylate and 2-hydroxypropyl (meth)acrylate.

(c) Glycidyl-containing vinyl monomers such as glycidyl (meth)acrylate and allyl glycidyl ether.

(d) Carboxy-containing vinyl monomers such as (meth)acrylic acid, itaconic acid and crotonic acid.

(e) (C₂₋₆ Alkenyl) esters of (meth)acrylic acid such as allyl (meth)acrylate.

(f) Vinyl aromatic compounds such as styrene, alpha-methylstyrene and vinyltoluene.

(g) Other vinyl monomers such as (meth)acrylonitrile, (meth)acrolein, butadiene and isoprene. These polymerizable unsaturated vinyl monomers may be used singly, or in combination with each other. Especially preferred among the above vinyl monomers are ethyl (meth)acrylates, butyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate and styrene.

35 Copolymerization

The polymerizable unsaturated polysiloxane compound (A), the polymerizable unsaturated alkoxy silane compound (B) and the polymerizable unsaturated vinyl monomer (C) are copolymerized with one another to form the vinyl-type copolymer in accordance with this invention. The proportions of the components (A), (B) and (C) may be set as follows.

Component	General range (wt.%)	Preferred range (wt.%)	Most preferred range (wt.%)
(A)	1-50	5-30	8-20
(B)	0-30	3-15	5-10
(C)	20-99	55-92	70-87

The weight percents (wt.%) of these components are based on the total weight of the three components (A), (B) and (C).

The copolymerization can be carried out by a radical polymerization method known *per se* in an inert organic solvent. Examples of the organic solvent that can be used in the copolymerization include esters such as ethyl acetate and butyl acetate; aromatic hydrocarbons such as benzene, toluene and xylene; ketones such as methyl ethyl ketone and methyl isobutyl ketone; alcohols such as isopropanol and butanol; and mixtures of two or more of these solvents. Radical polymerization initiators normally used in radical polymerization, for example benzoyl peroxide, azobisisobutyronitrile, lauroyl peroxide and cumene hydroperoxide, may be used in the copolymerization reaction.

The copolymerization reaction may be carried out at a temperature of about 80 to about 200°C, preferably about 100 to about 120°C, and can be terminated in 2 to 20 hours, preferably 5 to 10 hours, at these temperatures.

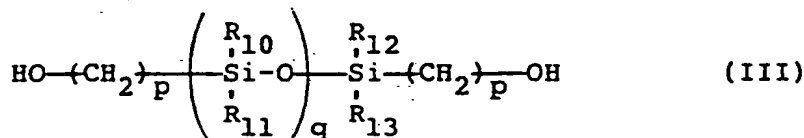
Advantageously, the vinyl-type copolymer produced by the above procedure generally has a weight average molecular weight (M_w) of about 3,000 to about 200,000, preferably about 5,000 to about 100,000, and a glass transition temperature (T_g) of -30 to 100°C, preferably -10 to 30°C.

65 Preparation of the paint composition

The paint composition of this invention can be prepared by dissolving or dispersing the vinyl-type copolymer so produced in a suitable solvent.

Solvents that are relatively volatile at ordinary temperature may be used for the preparation of the paint composition. Examples include ketones such as acetone and methyl ethyl ketone; esters such as ethyl acetate and butyl acetate; aromatic hydrocarbons such as benzene, toluene and xylene; alcohols such as isopropanol and butanol; petroleum solvent such as mineral spirit and aromatic petroleum naphtha; and mixtures of two or more of these solvents.

In addition to the vinyl-type copolymer, a siloxane compound having primary hydroxyl groups at both ends and represented by the following general formula



wherein

R_{10} , R_{11} , R_{12} and R_{13} are identical or different and each represents an alkyl group having 1 to 4 carbon atoms, an aryl group or an aralkyl group;

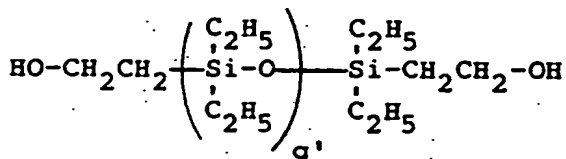
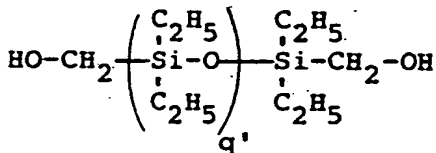
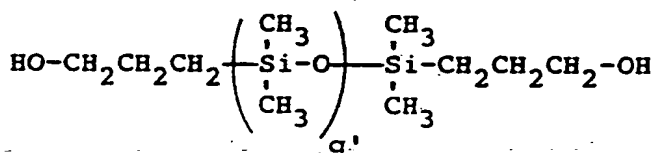
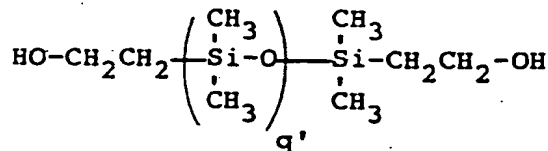
p is an integer of 1 to 5; and

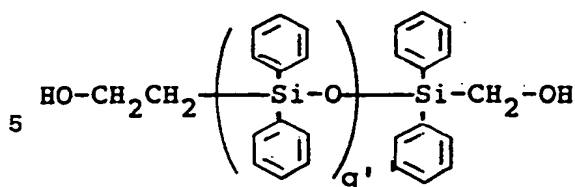
q is a number of 3 to 1,000,

may be incorporated in the paint composition of this invention. This can further increase the antifouling property of the composition.

Preferably in formula (III), R_{10} , R_{11} , R_{12} and R_{13} each represent a methyl group, p is in the range of 2 to 4, and q , which represents the average degree of polymerization of siloxane units, is 30 to 500, especially 50 to 300.

Specific examples of the siloxane compounds of formula (III) are given below.





$$q' = 30-500$$

Conveniently, the siloxane compound of formula (III) is included in an amount of generally 1 to 50 parts by weight, preferably 5 to 30 parts by weight, more preferably 8 to 20 parts by weight, per 100 parts by weight of the vinyl copolymer.

If further required, ordinary paint additives may be incorporated in the paint composition of this invention in amounts generally used. Examples of the paint additives are colored pigments such as red iron oxide, zinc oxide and chrome yellow, body extender pigments such as talc, clay and calcium carbonate, anti-corrosive pigments such as red lead, zinc chromate and lead chromate, plasticizers such as tricresyl phosphate, chlorinated paraffin and phthalates, and anti-aging agents such as finely divided silica, aluminum stearate and zinc stearate.

The antifouling paint composition of this invention may be prepared by mixing and dispersing the aforesaid components in a solvent by means of a dispersing device such as a ball mill and an attriter.

The amount of the vinyl-type copolymer in accordance with this invention is not strictly limited, and can be varied widely according to the type of a substrate to be coated by the paint composition or the site at which the substrate is located. Generally, it may be 15 to 70% by weight, preferably 30 to 50% by weight, based on the weight of the composition.

Utility

The antifouling paint composition provided by this invention gives a paint film having a low sliding friction angle and a low critical surface tension and therefore having excellent resistance to the adhesion of aquatic organisms. Its antifouling property is equivalent to, or higher than, that of a conventional antifouling paint of the type which releases a toxicant such as a metallic compound or an organometallic compound. In addition, the antifouling paint composition of this invention is very superior also as a nontoxic antifouling paint which permits easy removal of aquatic organisms that have adhered to the paint film.

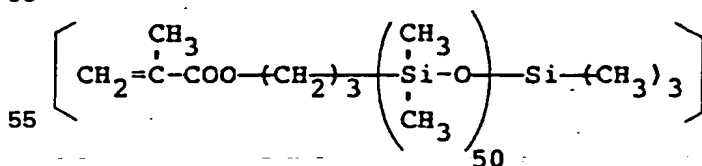
The antifouling composition of this invention can be used for coating the submerged parts of various ships and underwater and overwater structures such as cutting rigs, harbor docks, water gates and buoys.

The following examples illustrate the present invention further. It should be understood however that the invention is not limited to these examples alone, and various changes and modifications are possible without departing from the scope of the invention. In these examples, all parts and percentages are by weight unless otherwise specified.

PRODUCTION EXAMPLE 1

Production of a vinyl-type copolymer:-

In a reaction vessel, 20 parts of methacryloxypropylpolydimethylsiloxane of the following formula

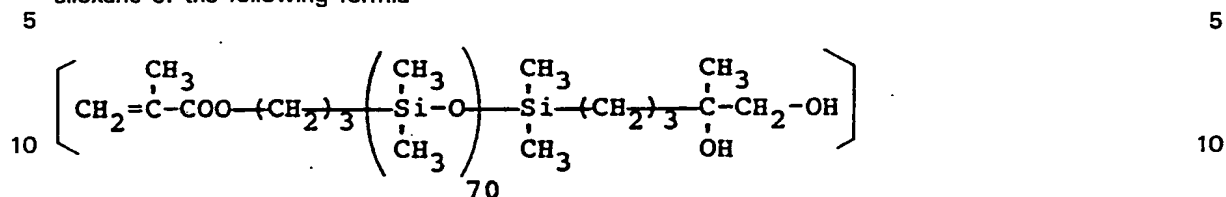


40 parts of methyl methacrylate and 40 parts of n-butyl methacrylate were dissolved in a 8:2 mixture of xylene and 40 parts of methyl methacrylate and 40 parts of n-butyl methacrylate were dissolved in a 8:2 mixture of xylene and butyl acetate, and 1.0 part of benzoyl peroxide was added. With stirring, the mixture was maintained at 90 to 100°C for 6 hours to give a solution of a vinyl-type copolymer having a Tg of 20°C and a weight average molecular weight of 30,000 in a solids concentration of 60%.

PRODUCTION EXAMPLE 2

Production of a vinyl-type copolymer:-

In a reaction vessel, 20 parts of methacryloxypropyl 4,5-dihydroxy-4-methylpentylpolydimethylsiloxane of the following formula



20 parts of methacryloxypropyltrimethoxysilane, 40 parts of isobutyl acrylate and 20 parts of styrene were dissolved in 67 parts of a 8:2 mixture of xylene and butyl acetate, and 0.5 part of azobisisobutyronitrile was added. With stirring, the mixture was maintained at 90 to 100°C for 6 hours to give a solution of a vinyl-type copolymer having a Tg of -10°C and a weight average molecular weight of 45,000 in a solids concentration of 60%.

20 PRODUCTION EXAMPLE 3

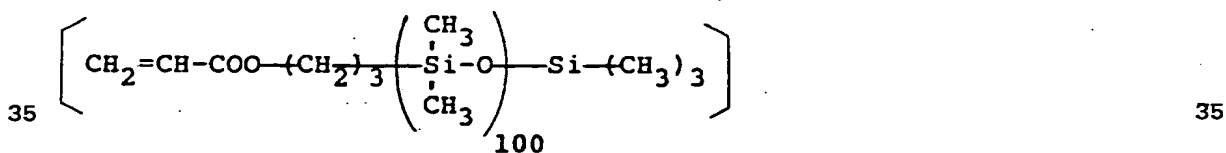
Production of a vinyl-type copolymer:-

Thirty parts of methacryloxypropylpolydimethylsiloxane used in Production Example 1, 30 parts of methacryloxypropyltrimethoxysilane and 40 parts of t-butyl methacrylate were polymerized by the same method as in Production Example 1 to give a solution of a vinyl-type copolymer having a Tg of 30 and a weight average molecular weight of 30,000 in a solids concentration of 60%.

PRODUCTION EXAMPLE 4

Production of a vinyl-type copolymer:-

In a reaction vessel, 30 parts of acryloxypropylpolydimethylsiloxane of the formula



10 parts of acryloxypropyltriethoxysilane, 30 parts of t-butyl methacrylate and 30 parts of isobutyl methacrylate were dissolved in 67 parts of an 8:2 mixture of xylene and butyl acetate, and 1.0 part of azobisisobutyronitrile was added. The mixture was maintained at 100 to 110°C for 6 hours to give a solution of a vinyl-type copolymer having a Tg of 14°C and a weight average molecular weight of 30,000 in a solids concentration of 30%.

EXAMPLE 1

Eighty parts of the vinyl-type copolymer solution obtained in Production Example 1, 0.5 part of Aerosil #200 (fine powder of silica produced by Degussa Company, West Germany) and 19.5 parts of xylene were mixed and dispersed by a paint conditioner to give an antifouling composition of this invention. A paint film prepared from it was tested for properties, and the results are shown in Table 2 below.

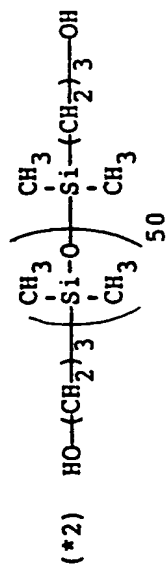
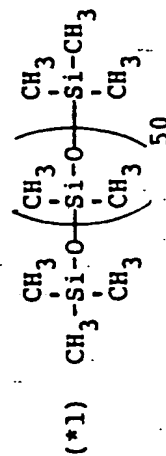
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EXAMPLES 2-8

In each run, an antifouling paint composition was prepared as in Example 1 in accordance with the mixing proportions shown in Table 1. The results of testing paint film properties are shown in Table 2.

Table 1

Materials	Example							
	1	2	3	4	5	6	7	8
Vinyl-type copolymer solution of Production Example 1	80.0				70.0			
Vinyl-type copolymer solution of Production Example 2		80.0				60.0		
Vinyl-type copolymer solution of Production Example 3			80.0				50.0	
Vinyl-type copolymer solution of Production Example 4				80.0		60.0		75.0
Silicone oil (*1)					8.0		4.0	
OH-containing silicon compound (*2)						14.0	16.0	3.0
Aerosil #200	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Xylene	19.5	19.5	9.5	19.5	21.5	25.5	14.5	21.5
Methyl isobutyl ketone			10.0				15.0	
Total (parts)	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0



COMPARATIVE EXAMPLES 1-4

Antifouling paint compositions were prepared in accordance with the following formulations, and the results of testing paint film properties are shown in Table 2.

5 Comparative Example 1

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	Parts
Vinyl chloride resin	10.0
Rosin	10.0
Tricresyl phosphate	4.0
10 Triphenyltin fluoride	10.0
Talc	5.0
Red iron oxide	5.0
Xylene	28.0
Methyl isobutyl ketone	28.0
15	
Total	100.0

15

20 Comparative Example 2

20

	Parts
Chlorinated rubber resin	5.0
Rosin	15.0
Tricresyl phosphate	4.0
Cuprous oxide	30.0
25 Talc	5.0
Baryta	3.0
Red iron oxide	4.0
Xylene	34.0
30	
Total	100.0

30

Comparative Example 3

	Parts
35 Vinyl chloride resin	5.5
Rosin	5.5
Tricresyl phosphate	2.0
Cuprous oxide	30.0
Triphenyltin hydroxide	10.0
40 Barium sulfate	4.0
Talc	11.0
Red iron oxide	10.0
Xylene	11.0
Methyl isobutyl ketone	11.0
45	
Total	100.0

45

Comparative Example 4

	Parts
50 Air-drying silicone resin	50
Xylene	50
55	
Total	100

50

55

Paint film property tests

A sand-blasted steel panel, 100×300×2 mm in size, was coated with a zinc-epoxy type shop primer (dry film thickness 15 microns) and an epoxy-type anticorrosive paint (dry film thickness 200 microns). Then, each of the paint compositions obtained in Examples 1 to 8 and Comparative Examples 1 to 4 was coated on the so-treated steel panel to a dry film thickness of 50 microns. The coated panel was dried for 7 days and then used in the following tests.

(1) Test of sliding friction of a water droplet

A water droplet (0.03 ml) was placed on the paint film. One end of the paint film was gradually lifted, and the angle of the coated sheet at the time when the water droplet began to

slide was measured.

(2) Measurement of the critical surface tension

The contact angles of water and paraffin in droplets were measured, and the critical surface tension of the coated surface was determined.

5 (3) Antifouling property test

The above test steel panel was immersed for 12 months in Toba Bay, Mie Prefecture, Japan, and the state of adhesion of organisms was examined. The numerical figures indicated in Table 2 are the percent area of adhesion.

10 The results given in Table 2 show that the antifouling paint composition of this invention had performance comparable to conventional paints containing cuprous oxide and organotin.

Table 2

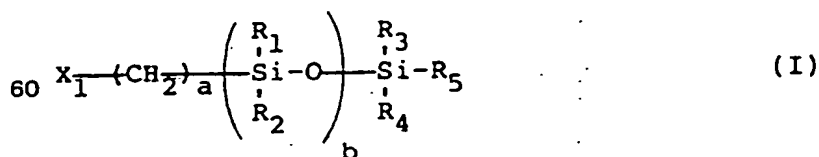
		Sliding friction angle (degrees)	Critical surface tension (dyne/cm)	Antifouling property	
				Green laver	Barnacle
Example	1	40	23.0	5	0
	2	20	20.5	0	0
	3	28.6	25.0	10	0
	4	25.3	21.8	1	0
	5	42	20.5	0	0
	6	12	18.4	0	0
	7	19	22.0	3	0
	8	24	23.5	0	0
Comparative Example	1	55	30.4	30	0
	2	45	32.1	5	2
	3	45	33.4	0	0
	4	60	18.8	10	30

The results given in Table 2 show that the antifouling compositions of this invention showed properties comparable to conventional paints containing cuprous oxide or organotin.

CLAIMS

1. An antifouling paint composition comprising as a film forming component a vinyl-type copolymer obtained by copolymerization of

(A) 1 to 50% by weight of a polymerizable unsaturated polysiloxane compound represented by the general formula



wherein

X₁ represents a group of the formula



where R₅ represents a hydrogen atom or a methyl group;

10 R₁, R₂, R₃ and R₄ are identical or different and each represents an alkyl group having 1 to 4 carbon atoms, an aryl group or an aralkyl group; 10

R₅ represents an alkyl group having 1 to 4 carbon atoms, or a hydroxyalkyl group having 1 to 3 hydroxyl groups and 1 to 6 carbon atoms;

a is 0 when X₁ represents the group



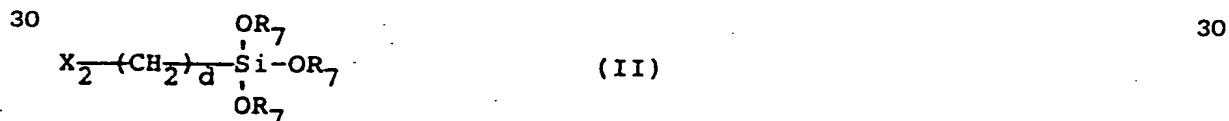
and an integer of 1 to 5 when X₁ represents the group



25 and 25

b is a number of 3 to 1,000,

(B) 0 to 30% by weight of a polymerizable unsaturated alkoxysilane compound represented by the general formula



35 wherein 35

X₂ represents a group of the formula



where R₆ represents a hydrogen atom or a methyl group;

45 R₇ represents an alkyl group having 1 to 4 carbon atoms; and 45

d is 0 when X₂ represents the group



and an integer of 1 to 5 when X₂ represents the group

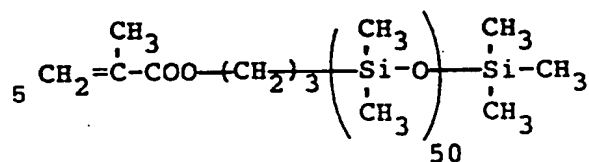


and

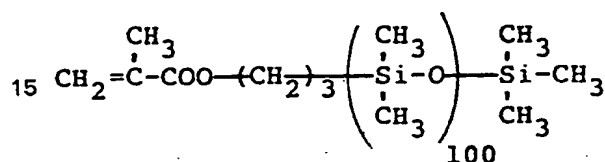
(C) 20 to 99% by weight of a polymerizable unsaturated vinyl monomer other than the compounds (A) and (B) above.

60 2. The composition of claim 1 wherein the polymerizable unsaturated polysilane compound (A) is a compound of general formula (I) in which R₁, R₂, R₃ and R₄ each represent a methyl group, R₅ represents a hydroxyalkyl group having 1 to 3 hydroxyl groups and 1 to 6 carbon atoms, and b is a number of 30 to 500. 60

65 3. A composition according to claim 1 wherein the polymerizable unsaturated polysilane compound (A) is 65



10 or



20 4. A composition according to claim 1, 2 or 3 wherein the polymerizable unsaturated alkoxy-silane compound (B) is selected from vinyltrimethoxysilane, vinyltriethoxysilane, vinyltripropoxysilane, vinyltributoxysilane, (meth)acryloxymethyltrimethoxysilane, (meth)acryloxyethyltrimethoxysilane, (meth)acryloxypropyltrimethoxysilane, (meth)acryloxypropyltriethoxysilane, (meth)acryloxyethyltriethoxysilane and (meth)acryloxypropyltributoxysilane. 20

25 5. A composition according to any one of the preceding claims wherein the polymerizable unsaturated vinyl monomer (C) is a compound containing 1 or 2 radical-polymerizable alpha, beta-ethylenically unsaturated bonds. 25

30 6. A composition according to claim 5 wherein the polymerizable unsaturated vinyl monomer (C) is selected from (C₁₋₁₂alkyl) esters of (meth)acrylic acid, hydroxy (C₂₋₆alkyl) esters of (meth)acrylic acid, glycidyl-containing vinyl monomers, carboxy-containing vinyl monomers, (C₂₋₆alkenyl) esters of (meth)acrylic acid and vinyl aromatic compounds. 30

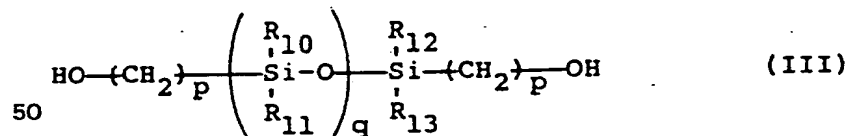
7. A composition according to claim 6 wherein the polymerizable unsaturated vinyl monomer (C) is selected from ethyl (meth)acrylate, butyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate and styrene.

35 8. A composition according to any one of the preceding claims wherein the vinyl-type copolymer is obtained by copolymerizing 5 to 30% by weight of the polymerizable unsaturated polysiloxane compound (A), 3 to 15% by weight of the polymerizable unsaturated alkoxy-silane compounds (B), and 65 to 92% by weight of the polymerizable unsaturated vinyl monomer (C). 35

40 9. A composition according to any one of the preceding claims wherein the vinyl-type copolymer has a weight average molecular weight of 3,000 to 200,000. 40

10. A composition according to any one of the preceding claims wherein the vinyl-type copolymer has a glass transition temperature of -30° to 100°C.

11. A composition according to any one of the preceding claims which further comprises a siloxane compound of the following general formula



wherein

55 1 to 4 carbon atoms, an aryl group or an aralkyl group; 55

p is an integer of 1 to 5; and

q is a number of 3 to 1,000.

12. A composition according to claim 11 wherein R₁₀, R₁₁, R₁₂ and R₁₃ each represent a methyl group, p is an integer of 2 to 4, and q is a number of 30 to 500.

60 13. A composition according to claim 11 or 12 which contains 1 to 50 parts by weight of the siloxane per 100 parts by weight of the vinyl-type copolymer. 60

14. A composition according to any one of the preceding claims which contains the vinyl-type copolymer in a concentration of 30 to 50% by weight.

65 15. A composition according to claim 1 substantially as described with reference to any one of Examples 1 to 8. 65

16. An antifouling coating derived from a composition as claimed in any one of the preceding claims on a surface of a ship or marine structure.

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